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964799

Date of Application and filing Complete Specification: April 7, 1961.
No. 12576/61.

Two Applications made in United States of America (Nos. 21884 and 21890)
on April 13, 1960.

Complete Specification Published: July 22, 1964.

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Index at acceptance:—C3 N4; B2 E(1A, 1H); B5 A(1R14C1X, 1R29X); B5 B(2A2B, 22A4)
C4 X5

International Classification:—C 07 g (B 29 d, f, C 09 j, D 01 f, D 06 m)

COMPLETE SPECIFICATION

Thermoplastic Amylaceous Compositions and their use in preparing Shaped or Coated Articles

We, HERCULES POWDER COMPANY, a Cor- still further object is to provide such a com- 45
pany, do hereby declare that the following is a full and complete description of the invention, which can be worked from a hot melt.

5

ERRATA

11

SPECIFICATION No. 964,799
Amendment No 1

1

Page 2, Table I, Pressure p.s.i. Column, for
"450" read "540" Example 1 and 2.
Page 3, Table 3, footnote (1), line 2, for
"210 SPC" read "210 cps"
Page 7, line 105, for "Ethers" read "Esters"

2

THE PATENT OFFICE
29th April 1966

25 bination of amylose and amylopectin or de-
gradation products therefrom.

30 In defining the compositions of this inven-
tion the amount of plasticizer is expressed
herein as per cent by weight of the derivative
of the amylose material as the derivative
is normally dried in preparation; such dried
derivatives contain about 1%—5% water. The
per cent water is expressed herein as per cent
by weight of the derivative of the amylose
35 material on an absolutely dry, i.e. water-free,
basis.

40 An object of the present invention is to
provide a composition which flows under heat
and pressure and which is water soluble. A
further object is to provide such a composi-
tion containing a derivative of an amylose
material, a plasticizer therefor and water, the
absolute amount of water being 1%—20% by
weight of said derivative on a dry basis. A

(e.g., alkylene oxide) or esterifying agent com-
bined per anhydroglucose unit of the starch
molecule and is determined by the familiar
Zeisel-Morgan method. 70

The following examples show a large
number of compositions and several articles
within the scope of this invention. In order
to determine how various such compositions
75 perform, the amount of plastic flow of the
composition was determined under the appli-
cation of heat and pressure in an Olson Bake-
lite Flow Tester. This is a standard testing
80 device widely used in the plastics industry. It
is described in ASTM method D 569—46A
(ASTM Standards, 1958, Part 9, page 393).
This device is perhaps more often referred
to in the art as the Tinius Olson Flow Tester. 85

For these plastic flow tests, very uniform
mechanism mixtures of the derivative and
plasticizer were made. By heat and pressure,

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International Classification:—C 07 g (B 29 d, f, C 09 j, D 01 f, D 06 m)

COMPLETE SPECIFICATION

Thermoplastic Amylaceous Compositions and their use in preparing Shaped or Coated Articles

We, HERCULES POWDER COMPANY, a Corporation organized under the laws of the State of Delaware, one of the United States of America, of 900 Market Street, City of Wilmington, Zone 99, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions which flow under heat and pressure and which are water soluble, and more particularly to such compositions comprising a derivative of an amylose material, a plasticizer therefor and water, said derivative being an ether, ester, mixed ether, mixed ester, mixed ether-ester, or a mixture of two or more thereof. One aspect of the invention relates to making various articles from said compositions.

By amylose material as used herein is meant any of the forms of starch, e.g. wheat, corn, sorghum, potato, tapioca, waxy maize, or amylose or amylopectin alone or any combination of amylose and amylopectin or degradation products therefrom.

In defining the compositions of this invention the amount of plasticizer is expressed herein as per cent by weight of the derivative of the amylose material as the derivative is normally dried in preparation; such dried derivatives contain about 1%—5% water. The per cent water is expressed herein as per cent by weight of the derivative of the amylose material on an absolutely dry, i.e. water-free, basis.

An object of the present invention is to provide a composition which flows under heat and pressure and which is water soluble. A further object is to provide such a composition containing a derivative of an amylose material, a plasticizer therefor and water, the absolute amount of water being 1%—20% by weight of said derivative on a dry basis. A

still further object is to provide such a composition which can be worked from a hot melt. Another object is a process of making various articles from such a composition comprising subjecting said composition to heat and pressure while maintaining said moisture content.

The above and other objects will become apparent from the description of this invention given hereinafter.

The above and other objects are accomplished according to the present invention by providing a composition which flows under heat and pressure and which is water soluble comprising (1) a derivative of an amylose material, (2) a plasticizer for said derivative, and (3) water, the amount of water being 1%—20% by weight of said derivative on a dry basis.

The following Examples illustrate various embodiments of the present invention, but it is not intended to limit the invention thereto except as defined in the claims. MS is used herein to mean the moles of etherifying agent (e.g., alkylene oxide) or esterifying agent combined per anhydroglucose unit of the starch molecule and is determined by the familiar Zeisel-Morgan method.

The following examples show a large number of compositions and several articles within the scope of this invention. In order to determine how various such compositions perform, the amount of plastic flow of the composition was determined under the application of heat and pressure in an Olson Bakelite Flow Tester. This is a standard testing device widely used in the plastics industry. It is described in ASTM method D 569—46A (ASTM Standards, 1958, Part 9, page 393). This device is perhaps more often referred to in the art as the Tinius Olson Flow Tester.

For these plastic flow tests, very uniform mechanism mixtures of the derivative and plasticizer were made. By heat and pressure,

the material was fused into a plastic mass. This mass was ground to a fine powder and conditioned generally at 25°C. and 50% R.H. for about 24 hours. Cylindrical pellets 3/8" x 3/8" were formed from this powder in a pelleting machine. The pellet was placed in the Tinius Olson Flow Tester and the plastic flow thereof measured under the conditions shown in the Examples.

The water content of the composition given herein was determined by a modification of the method described in Mitchell and Snell, *Aquametry*, pages 178—179, (1958), Interscience Publishers, New York City. Thus a 2.5 gram sample of the molding powder was mixed with enough methanol to fill a 100 ml. volumetric flask. This was allowed to stand at about 25°C. for 45 minutes. Then an aliquot was analyzed by the Johansson modification of the Karl Fischer method (see the above Mitchell and Snell reference).

In the following tables various abbreviations are used as a matter of convenience.

HES is hydroxyethyl starch
HPS is hydroxypropyl starch
HPA is hydroxypropyl amylose

HEAP is hydroxyethyl amylopectin
HPAP is hydroxypropyl amylopectin
CMS is carboxymethyl starch
CMA is carboxymethyl amylose
CMAP is carboxymethyl amylopectin
AS is acetyl starch
AA is acetyl amylose
AAP is acetyl amylopectin
Methyl S is methyl starch
MA is methyl amylose
MAP is methyl amylopectin
CMHPS is carboxymethyl hydroxypropyl starch
MHPS is methyl hydroxypropyl starch
AHPS is acetyl hydroxypropyl starch
The amylopectin derivatives were prepared from a commercial grade of waxy maize starch. The amylose derivatives were prepared from a commercial grade of amylose obtained by fractionation of potato starch. All derivatives prepared from starch, i.e. HPS, HES, CMS, AS, Methyl S, CMHPS, MHPS, and AHPS were prepared from a commercial grade of wheat starch containing about 25% amylose and 75% amylopectin.

EXAMPLES 1—8 (Table 1)

Effect of MS

Example No.	Derivative Type	MS	Plasticizer		H ₂ O % ⁽¹⁾	Extrusion		Flow inches/2 mins.
			Type	Amt. %		Temp. °C.	Pressure p.s.i.	
1	HPS	0.13	Propylene glycol	10		120	450	0.49
2	HPS	0.23	"	10		100	450	1.1
3	HPS	0.44	"	10		100	540	1.4
4	HPS	0.58	"	10		100	540	1.8
5	HPA	0.26	"	10		150	540	0.56
6	HPA	0.42	"	10		150	540	0.92
7	HPAP	0.21	"	10		100	340	0.66
8	HPAP	0.34	"	10		100	340	1.02

⁽¹⁾ Plasticized derivatives conditioned at 50% R.H. and 25°C. for 24 hours and flow tested immediately.

EXAMPLES 9—13 (Table 2)

Effect of Water

Example No.	Derivative Type	MS	Plasticizer		H ₂ O %	Extrusion		Flow inches/2 mins
			Type	Amt. %		Temp. °C.	Pressure p.s.i.	
9	HPS	0.58	Propylene Glycol	20	1.4	100	540	1.5
10	HPS	"	"	"	3.6	"	"	5.5
11	HPS	0.44	"	"	2.7	"	"	1.0
12	HPS	"	"	"	6.3	"	"	5.9
13	HPS	"	Glycerol	"	7.1	"	"	5.5

EXAMPLES 14—22 (Table 3)

Use of Various Plasticizers

Example No.	Derivative Type	MS	Plasticizer		H ₂ O % ⁽¹⁾	Extrusion		Flow inches/2 mins.
			Type	Amt. %		Temp. °C.	Pressure p.s.i.	
14	HPS	.44	Propylene glycol	10		100	540	1.4
15	HPS	"	Diethylene glycol	"		"	"	1.7
16	HPS	"	Dipropylene glycol	"		"	"	0.50
17	HPS	"	Monoacetyl glycerol	"		110	"	0.72
18	HPS	"	Diacetyl glycerol	"		"	"	0.70
19	HPS	"	Hydroxypropyl glycerol	"		"	"	0.52
20	HPS	"	Aminoethyl ethanolamine	"		"	"	0.77
21	HPS	"	Methyl di-ethanolamine	"		"	"	0.73
22	HPS	"	Glycerol	"		100	"	2.1

⁽¹⁾ Plasticized derivatives conditioned at 50% R.H. and 25°C. for 24 hours and flow tested immediately. In each example the HPS had a viscosity of 210 SPC. measured at 5% solids concentration in aqueous solution at 25°C. with a Brookfield Viscometer.

EXAMPLES 23—33 (Table 4)
Various Amounts of Plasticizer

Example No.	Derivative Type	MS	Plasticizer		H ₂ O %	Extrusion		Flow inches/2 mins.
			Type	Amt. %		Temp. °C.	Pressure p.s.i.	
23	HPS	0.13	Propylene glycol	10	(¹)	120	540	0.49
24	HPS	„	„	20	„	„	„	3.0
25	HPS	„	Dipropylene glycol	10	„	„	„	0.16
26	HPS	„	„	20	„	„	„	0.67
27	HPS	0.58	Propylene glycol	20	„	100	„	5.5
28	HPS	0.28	Dipropylene glycol	10	„	„	„	0.14
29	HPS	„	„	20	„	„	„	0.47
30	HPS	„	Diethylene glycol	10	(²)	„	„	0.37
31	HPS	„	„	20	„	„	„	1.5
32	HPS	„	Glycerol	10	„	„	„	0.28
33	HPS	„	„	20	„	„	„	Too soft

(¹) Plasticized derivatives conditioned at 50% R.H. and 25°C. for 24 hours and flow tested immediately.

(²) Plasticized derivatives conditioned at 20% R.H. and 25°C. for 24 hours and flow tested immediately.

EXAMPLES 34—38 (Table 5)

Effect of Viscosity

Example No.	Derivative	Viscosity ⁽¹⁾ cps.	MS	Plasticizer		H ₂ O % ⁽²⁾	Extrusion		Flow inches/2 mins.
	Type			Type	Amt. %		Temp. °C.	Pressure p.s.i.	
34	HPS	150	0.50	Propylene glycol	10		100	540	1.08
35	HPS	125	"	"	"		"	"	1.28
36	HPS	50	"	"	"		"	"	1.49
37	HPS	16.5	"	"	"		"	"	1.65
38	HPS	7.0	"	"	"		"	"	5.3

(¹) Measured at 5% solids concentration in aqueous solution at 25°C. with a Brookfield Viscometer i.e., viscosity of 5% aqueous solution of the derivative.

(²) Plasticized derivatives conditioned at 50% R.H. and 25°C. for 24 hours and flow tested immediately.

EXAMPLES 39—54 (Table 6)

Use of Various Derivatives of Amylaceous Materials

Example No.	Derivative Type	MS ⁽¹⁾		Plasticizer		Extrusion		Flow inches ² /2 mins.
				Type	Amt. %	Temp. °C.	Pressure p.s.i.	
39	HPS	0.28		Propylene glycol	10	100	540	1.13
40	HPA	0.21		"	"	150	"	0.56
41	HPAP	0.26		"	"	100	340	0.66
42	CMS	0.87		"	20	"	540	3.8
43	CMA	1.05		"	"	150	"	0.21
44	CMAF	0.7		"	"	100	"	1.8
45	AS	0.44		"	10	"	"	2.0
46	AA	0.65		"	"	150	"	0.83
47	AAP	0.32		"	"	100	"	1.7
48	Methyl S	0.50		"	"	"	"	1.6
49	Methyl A	0.75		"	"	150	"	2.6
50	Methyl AP	0.39		"	"	100	"	2.1
51	HES	1.15		"	20	"	"	11.0
52	CMHPS	0.10	0.19	"	10	"	"	0.42
53	MHPS	0.25	0.24	"	"	"	"	1.0
54	AHPS	0.20	0.10	"	"	"	"	0.31

(¹) For the mixed derivatives the MS of each substituent is given in the order in which the derivative is named, e.g. the MS for the CMHPS means a carboxymethyl MS of 0.10 and a hydroxypropyl MS of 0.19.

The absolute water content of each composition was 4.5% by weight of the derivative.

The above Examples show the effect of a number of variables on this invention. Examples 1—8 (Table 1) show that the plastic flow increases with increase in the MS of the derivative used in the composition. Examples 9—13 (Table 2) show that the plastic flow increases with increase in the water content of the composition. It was found that water is a necessary ingredient of the composition. While from 1%—20% water by weight of the starch derivative on an absolute dry basis may be used, it is preferably to use from 3—8% of water. It is necessary to retain the moisture content within the 1%—20% range (preferably 3%—8%) during extrusion or other means of making useful articles from the composition. For example, it is necessary that the extruder be unvented. As contrasted with this it has been found that the use of hot two-roll mills, as commonly used in the art for processing other thermoplastic materials, is not satisfactory and forms a very brittle product because the water flashes off during processing.

Although a plasticizer is a necessary ingredient in the compositions in order for the compositions to be commercially attractive, the amount of plasticizer may vary widely and various amounts and numerous types of plasticizers have been successfully used. In general, while better results were obtained with the plasticizers in Examples 14—22 and 23—33 (Tables 3 and 4 above), there have also been successfully used as plasticizers according to this invention hydroxyethyl morpholine, butyl carbitol and polyoxyethylene. As to amount of plasticizer, excellent results have been obtained with compositions containing 10%—20% plasticizer by weight of the derivative of the amylaceous material. Amounts outside this range of plasticizer may be used. For instance, for some commercial operations where very rapid flow rates are economically desirable, one may use amounts of plasticizer considerably greater than 20% (see Examples 55—57 hereinafter).

Examples 34—38 (Table 5) show that plastic flow increases with decrease in viscosity of the derivative. However, the outstanding advantage of this invention is realized irrespective of the viscosity of the derivative. That is, whether the viscosity of the derivative is low or high, in making shaped articles the compositions of the invention are employed as a hot melt instead of an aqueous solution. In fact, aqueous solutions cannot be efficiently made into the shaped articles of this invention. Large amounts of water would have to be evaporated when using a solution. This would be commercially unacceptable not only from the standpoint of cost of removing the tremendous amount of water but also from the standpoint of drastically limiting the rate of making shaped articles from aqueous solutions.

The prior art has provided the derivatives

used in this invention in various degrees of degradation. The prior art has used various means of degradation, including acid hydrolysis, oxidation, heat, light, high energy radiation, and enzymes. The means used to degrade the derivatives is immaterial insofar as the nature of the degraded product is involved, and all such means are applicable in the invention. The hydroxypropyl starch derivatives in Table 5 above were degraded by oxidation to the viscosities shown.

Some variation in flow may be obtained by varying the amount and type of plasticizer. However, it is preferred to control with plasticizer the shaped article properties of flexibility, and resistance to curl, blocking and cracking, and to control with temperature and pressure the flow of the composition in making the shaped articles. Variation of the MS of the derivative may be used to control flow and also the above-mentioned properties of the shaped articles.

Examples 39—54 (Table 6) show the use of a large number of derivatives of amylaceous materials in accordance with this invention. However, the invention is applicable to derivatives of amylaceous materials broadly as defined hereinbefore. These include, e.g., the following water-insoluble derivatives of amylaceous materials.

I. Ethers

1. Saturated alkyl, including, e.g. methyl, ethyl, propyl
2. Unsaturated alkyl, e.g., vinyl, allyl
3. Hydroxyalkyl, e.g., hydroxyethyl, hydroxypropyl
4. Carboxyalkyl, e.g., carboxymethyl, carboxyethyl, carboxypropyl
5. Cyanoalkyl, e.g., cyanoethyl

II. Ethers

1. Saturated fatty acid, e.g., acetyl, propionyl
2. Unsaturated fatty acid, e.g., acrylyl

III. Mixed derivatives comprising two or more of the ethers and/or esters in I and II above. Typical mixed derivatives are the carboxymethyl hydroxypropyl, methyl hydroxypropyl, ethyl hydroxyethyl, acetyl hydroxypropyl derivatives.

Water-soluble acyl derivatives of amylaceous materials are applicable as a class to the present invention, the saturated and unsaturated fatty acid esters as well as the acetyl hydroxypropyl derivatives listed immediately above being typical examples of these acyl derivatives.

Table 7 hereinafter gives the broad and preferred MS ranges applicable to this invention. As one exceeds the preferred maximum MS the benefits realised from increased MS begin to level off, especially the hydroxyalkyl and carboxyalkyl derivatives. In the case of the alkyl and acetyl derivatives, one should not exceed an MS of about 1.5 because the product becomes less water soluble and more

organosoluble such that at an MS of about 2 they are water insoluble and organosoluble and this would eliminate one of the chief advantages of the present invention.

TABLE 7

Broad and Preferred MS Ranges

Derivative	Amylopectin		Amylose-Amylopectin Mixture ⁽¹⁾		Amylose	
	Broad MS	Preferred MS	Broad MS	Preferred MS	Broad MS	Preferred MS
Hydroxy-alkyl	At least 0.1	0.2—0.6	At least 0.1	0.2—0.6	At least 0.3	0.5—1.0
Carboxy-alkyl	At least 0.5	0.8—1.5	At least 0.5	0.8—1.5	At least 1.0	1.2—1.8
Alkyl	0.3—1.5	0.5—1.2	0.3—1.5	0.5—0.8	0.6—1.5	0.8—1.2
Acetyl	0.3—1.5	0.5—1.2	0.3—1.5	0.5—0.8	0.6—1.5	0.8—1.2

⁽¹⁾ About 25% amylose—75% amylopectin mixture as usually appears in most starches.

This invention has a large number of applications wherein it excels. It may be used wherever there is a need for coated or shaped articles, e.g., paper, filaments, films, sheets, rods, tubes, capsules and containers in general or other such articles. Filaments, films, sheets, rods and tubes may be produced by extrusion of the composition of the invention through an orifice, while capsules may be produced by compression molding or injection molding.

A very desirable property for many applications, which it has been found that the articles made from the compositions of this invention possess, is that of heat sealability. That is, by the application of slight pressure and heat, the material permanently heat seals or adheres to itself and various other materials. The following Examples 55—59 are specific applications of these.

EXAMPLES 55—57 (Films, Rods and Filaments)

In order to prepare shaped articles in the form of films, a sample of hydroxypropyl amylose of 0.50 MS was intimately mixed with 50% propylene glycol by weight of the hydroxypropyl amylose. This was allowed to condition for 18 hours at 25°C. and 50% R.H. The resulting rubbery mass, which contained about 8% water, was extruded through a one-inch United States Rubber Machine extruder fitted with a 2-inch long slit 10 mils wide to form films. The films were extruded at a temperature of 300°F. and 52 r.p.m. screw speed. The films were smooth, colorless, tough, flexible and transparent. The thickness of the films varied from 6 to 2 mils depending on how much tension the films were subjected to during extrusion.

In order to prepare shaped articles in the

form of rods, some of the extruded films were recycled through the extruder using a 1/16" diameter circular orifice at 250°F. and 32 r.p.m. screw speed. The rods had excellent flexibility and strength.

By applying tension to the rods during extrusion, which was done by winding the rods around a spindle, the rods were drawn down to very fine filaments. These filaments had excellent flexibility and strength.

EXAMPLE 58 (SHEETS)

In order to prepare shaped articles in the form of sheets a sample of hydroxyethyl starch of 0.89 MS was intimately mixed with 3% propylene glycol by weight of the hydroxypropyl starch. This was allowed to condition for 24 hours at 25°C. and 50% R.H. The resulting powdery mass, which contained about 8% water, was compression molded for three minutes between polished metal plates at 220°F. and 300 p.s.i. After cooling the molds to about 110°F. the molded sheets were removed. The molded sheets were about 10 mils thick, clear, smooth and transparent.

EXAMPLE 59 (SHEETS)

Sheets were prepared as in Example 58 above using hydroxyethyl amylose of 0.50 MS and a molding temperature of 300°F. The sheets had substantially the same properties as the sheets of Example 58 but were significantly tougher.

Although all of the compositions of this invention are useful in making all of the shaped articles of this invention, for making shaped articles in which one desires high tensile strength and flexibility, it is preferred to use compositions wherein the amyloseous material from which the derivative is made

contains about 50%—90% amylose. The amylose-rich starches may be obtained by any of the standard methods of fractionation whereby the amylose and amylopectin in starches are separated, such as for example the fractionation method disclosed in P. G. Schoch, *Advances in Carbohydrate Chemistry* edited by W. W. Pigman and M. L. Wolfrom, page 247 (1945), Academic Press, New York City. Excellent results have been obtained with a commercial product which contains approximately 90% amylose and 10% amylopectin and was obtained by fractionating potato starch. Also equally applicable are several other high amylose content starches which have recently become available.

Compositions containing derivatives of amylaceous materials have been used heretofore in the coatings field; however, their use has been quite limited because of certain drawbacks. One very serious drawback is that such coatings have been applied from aqueous solutions thereof. Under the conditions of applying the coatings, solutions of said derivatives are very viscous, so that the maximum concentration of solution is very low and much water must be evaporated in applying the coatings, thus presenting a serious commercial disadvantage not only from the standpoint of cost of removing the tremendous amount of water but also from the standpoint of limiting the rate at which the coatings may be applied to an object. One contribution of merit which the art has made toward solving this problem, although it has by no means solved the problem, is to degrade the starch derivative by various means (e.g. acid hydrolysis, oxidation, heat, light, high energy radiation, and enzymes) so that the viscosity is reduced sufficiently to enable the preparation of aqueous solutions of higher solids concentrations, say 50%—60%. While this is a substantial improvement over using the lower concentration solutions, it still entails the very serious drawback of application of the coatings from an aqueous solution.

Articles are coating according to this invention by subjecting the coating composition to heat and pressure during application of the coating, thereby causing the composition to flow, and maintaining the water content of the coating composition during application of the coating.

The following Examples illustrate various embodiments of the present invention. Viscosity as disclosed in this application was measured at 5% solids concentration of the derivative in aqueous solution at 25°C. with a Brookfield Viscometer.

While this invention is applicable to coating articles in general, for example, paper, fabric, filaments, films, sheets, rods, tubes, capsules and containers, it has been found to be especially applicable to coating sheet materials such as paper, fabric, and plastic articles. The following examples illustrate these applications.

EXAMPLES 60—65 (TABLE 8) *Coating Paper*

In these examples paper was coated with several derivatives of amylaceous materials under various conditions as to coating compositions and conditions of applying the coating. In each case a rewettable, heat-sealable, flexible, glossy, smooth and colorless coating was applied which adhered well to the paper. In each example the derivative and plasticizer were uniformly mixed. The mixture was conditioned at 50% relative humidity and 25°C. for 24 hours and used immediately for coating. Thus, the resulting compositions were extruded through a 0.01" x 2" die opening of a 1" U.S. Rubber Machine Company extruder. The extruder was operated at the temperature shown in Table 8 below and at a screw speed of 56 r.p.m. A continuous length of paper was coated with the compositions being extruded in the form of a ribbon by allowing the ribbon to be extruded onto the paper as the paper was passed about 1/32" below the die in the direction of the extrusion. By operating with the speed of the paper greater than that of the ribbon, the ribbon was stretched such that coatings only 2 mils thick and 2" wide were applied to the paper. The coated paper adhered well to various other objects when the coatings were moistened and placed in contact with such objects, thus showing its utility in commercial type gummed tapes. The coated paper also adhered well to itself and to another piece of paper when pressed in contact therewith and heated.

Further details are given in Table 8 which follows.

TABLE 8 (Examples 60—65)

Ex.	Coating Paper				Extrusion				
	Derivative			Plasticizer		H ₂ O %	Temp. °F.	Screw Speed RPM	Coating Thickness Mils
	Type	MS	Viscosity cps.	Type	Amt. %				
60	HPS ⁽¹⁾	0.13	830	Propylene glycol	60	11.7	250—270	56	2
61	"	0.23	1110	"	"	10.3	230—250	"	"
62	"	0.31	530	"	"	9.0	"	"	"
63	HPA	0.5	90	"	50	(²)	300	"	"
64	HEAP	0.4	5	"	"	"	250—280	"	"
65	AAP	0.8	10	"	"	"	260—280	"	"

(¹) Made from wheat starch of about 25% amylose and 75% amylopectin.

(²) Plasticized derivative conditioned at 50% R.H. and 25°C. for 24 hours and used immediately for coating

EXAMPLES 66 AND 67 (TABLE 9) Coating Fabric and Plastic

5 In Example 66 an 80 × 80 cotton print cloth was coated with acetylated starch. In Example 67 a film of linear poly(propylene) was coated with hydroxyethyl starch. These coatings were applied under substantially the same conditions and substantially the same results were obtained as in Examples 60—65 above, ex-

cept as otherwise indicated. The coating reduced the oxygen and hydrocarbon permeability of the polypropylene film. If desired, in order to increase the penetration of the coating into the cloth the coated cloth may be passed between heated rolls. Further details are given in Table 9 which follows.

TABLE 9 (Examples 66—67)

Ex.	Coating Fabric and Plastic				Extrusion				
	Derivative			Plasticizer		H ₂ O %	Temp. °F.	Screw Speed RPM	Coating Thickness Mils
	Type	MS	Viscosity cps.	Type	Amt. %				
66	AS ⁽¹⁾	0.9	10	Glycerol Monoacetate	25	(²)	280	56	1
67	HES ⁽¹⁾	0.4	150	Glycerol	30	(²)	250	56	0.2

(¹) Made from wheat starch of about 25% amylose and 75% amylopectin.

(²) Plasticized derivative conditioned at 50% R.H. and 25°C. for 24 hours and used immediately for coating.

20 As those skilled in this art will appreciate, the specific conditions given hereinbefore for preparing the coated articles may be varied

considerably within the present invention as defined in the appended claims.

While it is necessary in coating articles

according to this invention to subject the coating compositions to heat and pressure in order to cause the compositions to flow and thus take advantage of this very valuable property of the compositions, the temperature and pressure may vary appreciably. Temperature and pressure vary inversely, i.e. the higher the temperature, the lower the pressure required, and conversely. Good results have been obtained within the range of 200°F.—350°F. and 50—10,000 p.s.i. For most applications, 230°F.—280°F. and 100—500 p.s.i. are preferred. Broadly, then, applicable temperatures and pressures may range from those at which the coating compositions being applied will flow to just short of the temperatures at which either the coating compositions or articles being coated are adversely affected such as deforming the articles being coated or decomposing the articles being coated or the coating compositions.

This invention is applicable to coating any article which is not harmed by the temperatures necessary for causing the coating compositions to flow.

As is well known, there are numerous uses for coated paper other than the gummed tape mentioned above, although the gummed tape use is very large. For instance, enamel floor coverings normally contain asphalt-impregnated paper (often referred to as a felt base) attached to the underside of the enamel covering. One serious difficulty which the art has experienced with such floor coverings is the migration of the asphalt through the enamel covering. A thin film of the composition of this invention applied between the enamel covering and the felt base eliminates this migration. The compositions of this invention are useful in coating cloth for the purpose of making gummed cloth for use in the manufacture or repairing of books and the like, and for making prepasted cloth-based wall-paper (sometimes referred to as oilcloth). These compositions are also useful as cloth stiffening agents and as a backing for rugs. If desired, the compositions of this invention may be used to coat other plastic articles besides linear polypropylene, and it has been found that they have good adhesion to plastic articles in general. For instance, excellent results have also been obtained in coating poly(ethylene glycol terephthalate) with said compositions. One very desirable property imparted to articles by coating them with the compositions of this invention is that of substantially reduced permeability to oxygen and hydrocarbons. This renders such coated articles much more suitable for wrapping objects containing these materials or making articles for packaging them.

This invention is applicable to coating articles with the compositions defined herein irrespective of the viscosity of the derivative employed in said compositions. Also, it is im-

material what means are employed to obtain the desired viscosity. That is, whether the viscosity of the derivative is low or high, articles are coated according to the invention using a hot melt of the composition instead of an aqueous solution thereof. In fact, coatings cannot be efficiently applied from aqueous solutions of these compositions. Large amounts of water would have to be evaporated when using aqueous solutions. This would be commercially unacceptable not only from the standpoint of cost of removing the tremendous amount of water but also from the standpoint of drastically limiting the rate at which the articles could be coated.

As those skilled in this art will appreciate, various additional materials may be used with the compositions of this invention. These additional materials include, e.g., clay, pigments, fillers in general, dyes.

Likewise, the artisan will know that the various conventional techniques of preparing shaped articles and coated articles are applicable in the invention; these techniques include, e.g., compression molding, injection molding, and extrusion.

WHAT WE CLAIM IS:—

1. A composition which flows under heat and pressure and which is water soluble comprising (1) a derivative of an amylaceous material as defined herein, (2) a plasticizer for the derivative, and (3) water, the absolute amount of water being 1%—20% by weight of the derivative on a dry basis, said derivative being an ether, ester, mixed ether, mixed ester or mixed ether-ester, or a mixture of two or more thereof.
2. A composition according to Claim 1 wherein the derivative is a hydroxyalkyl derivative.
3. A composition according to Claim 1 wherein the derivative is a carboxyalkyl derivative.
4. A composition according to Claim 1 wherein the derivative is an alkyl derivative.
5. A composition according to Claim 1 wherein the derivative is a mixed carboxyalkyl hydroxyalkyl derivative.
6. A composition according to Claim 1 wherein the derivative is a mixed alkyl hydroxyalkyl derivative.
7. A composition according to Claim 1 wherein the derivative is a cyanoalkyl derivative.
8. A composition according to Claim 1 wherein the derivative is an acyl derivative.
9. A composition according to Claim 1 wherein the derivative is a mixed acyl hydroxyalkyl derivative.
10. A process for making shaped articles which comprises subjecting a composition according to any one of Claims 1 to 9 in the form of a hot melt to the influence of heat and pressure while maintaining its water content.

11. A process according to Claim 10 wherein the shaped article is a filament, rod, tube, sheet, or film and is formed by extruding the composition through an orifice.
- 5 12. A process according to Claim 10 wherein the shaped article is a capsule and is formed by compression molding or injection molding the composition.
- 10 13. A process for coating articles which comprises applying a composition according to any one of Claims 1 to 9 to the article under the influence of heat and pressure, thereby causing the composition to flow, and maintaining the water content of the composition during application.
- 15 14. A process according to Claim 13 wherein the temperature of the composition employed during application of the coating is 200°F.—350°F. and the pressure is 50—10,000 p.s.i.
- 20 15. A process according to Claim 13 or 14 wherein the article being coated is paper, fabric, plastic, or polypropylene film.
- 25 16. A process according to Claim 13, 14 or 15 wherein the composition contains an acetylated amylose derivative.
17. Compositions according to Claim 1 and substantially as herein described with especial reference to Examples 1—54.
18. Processes according to Claim 10 for making shaped articles, substantially as herein-described with especial reference to Examples 55—59.
19. Processes according to Claim 13 for coating articles, substantially as herein-described with especial reference to Examples 60—67.
20. Shaped articles produced by processes according to any of Claims 10, 11, 12 and 18.
21. Coated articles produced by processes according to any of Claims 13, 14, 15, 16 and 19.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press
(Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings,
London, W.C.2, from which copies may be obtained.

